

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>3</sup>:</b> <b>B01D 53/04</b>	<b>A1</b>	<b>(11) International Publication Number:</b> WO 81/02256 <b>(43) International Publication Date:</b> 20 August 1981 (20.08.81)
<b>(21) International Application Number:</b> PCT/US81/00144 <b>(22) International Filing Date:</b> 3 February 1981 (03.02.81)  <b>(31) Priority Application Number:</b> 118,554 <b>(32) Priority Date:</b> 4 February 1980 (04.02.80) <b>(33) Priority Country:</b> US  <b>(71) Applicants; and</b> <b>(72) Inventors:</b> UNDERHILL, Dwight, W. [US/US]; 5700 Centre Avenue, Pittsburgh, PA 15206 (US). LASKIE, James, R. [US/US]; 23 MacArthur Road, Wellesley, MA 02181 (US).  <b>(74) Agents:</b> BROOK, David, E. et al.; Hamilton, Brook, Smith & Reynolds, 2 Militia Drive, Lexington, MA 02173 (US).		<b>(81) Designated States:</b> BR, DE (European patent), FR (European patent), GB (European patent), JP.  <b>Published</b> <i>With international search report</i>
<b>(54) Title:</b> IMPREGNATED CHARCOAL FOR REMOVING RADIOACTIVE MOLECULES FROM GASES  <b>(57) Abstract</b> <p>Impregnated adsorbent for removing radioactive molecules from gas wherein charcoal is impregnated by spraying or other simple techniques with a substituted 1,4-diazabicyclo[2.2.2]octane which is a liquid at atmospheric pressure and a range of normal operating temperatures.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	KP	Democratic People's Republic of Korea
AU	Australia	LI	Liechtenstein
BR	Brazil	LU	Luxembourg
CF	Central African Republic	MC	Monaco
CG	Congo	MG	Madagascar
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SE	Sweden
FR	France	SN	Senegal
GA	Gabon	SU	Soviet Union
GB	United Kingdom	TD	Chad
HU	Hungary	TG	Togo
JP	Japan	US	United States of America

-1-

IMPREGNATED CHARCOAL FOR REMOVING  
RADIOACTIVE MOLECULES FROM GASES

Description

Technical Field

- 5        This invention is in the field of adsorbent materials for removing radioactive molecules, such as methyl iodide, from gases.

Background Art

- 10       It is often necessary to trap or remove radioactive molecules from gases. This is particularly true regarding nuclear energy plants, where off-gas streams often contain radioactive molecules, including alkyl halides such as methyl iodide. Such radioactivity is usually caused by isotopes, such as iodine 131.

- 15       A common method employed for removing radioactive molecules from such gas streams involves the use of gas filtration systems containing beds of adsorbent materials, such as charcoal. When used in this capacity, charcoal is frequently treated to  
20       increase its surface area; such treated charcoal is frequently called activated charcoal, and is intended to be included within the term charcoal as used herein. Such adsorbent beds are normally operated at room temperatures although they must be capable of with-  
25       standing higher temperatures under emergency conditions.

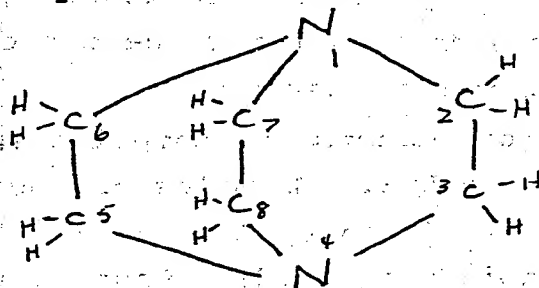
      To increase the adsorption efficiency of such beds, the adsorbent may be impregnated with substances



-2-

that increase its tendency to adsorb certain molecules such as alkyl halides. Examples of impregnants previously used with activated charcoal for this purpose are set forth in U.S. Patent No. 3,453,807, issued 5 to R. Taylor in 1969.

In the Taylor patent, activated charcoal is impregnated with a water-soluble secondary or tertiary amine. One such tertiary amine (referred to in the claims as a secondary amine) is stated to be triethyl-  
10 enediamine (TEDA), which might also be named 1,4-diazabicyclo[2.2.2]octane. This substance can be represented by the following chemical formula:

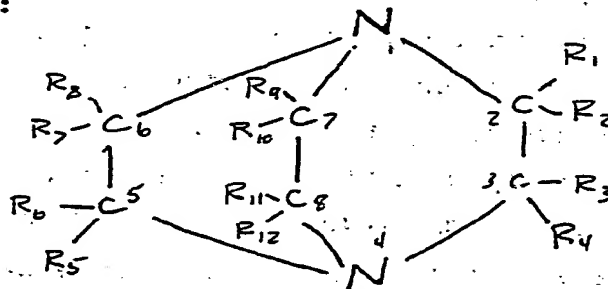


While 1,4-diazabicyclo[2.2.2]octane has proven  
15 to be somewhat suitable for trapping radioactive alkyl halides and other molecules, it suffers from several disadvantages. One significant disadvantage is that this substance is a crystalline solid at atmospheric pressure and normal operating temperatures. Therefore,  
20 it must be dissolved in a solvent, such as water, prior to application to the charcoal. This has proven to be a complex and troublesome operation in the production of impregnated charcoal. In addition, this substance tends to be relatively volatile. Therefore, it tends  
25 to escape from impregnated charcoal through the process of sublimation.

1,4-diazabicyclo[2.2.2]octane can be modified to render it a liquid at atmospheric pressure over a substantial range of temperatures. This can be accomplished by substituting any of several groups for  
30 one of the hydrogen atoms on the 1,4-diazabicyclo[2.2.2]-

octane. Such appended groups disrupt the symmetrical shape of the unsubstituted molecules, reducing its tendency to crystallize. Such substituted compounds can be represented by the following structural

5: formula:



wherein the combination of R substituents, one or more of which are not hydrogen, cause the compound to be a liquid at atmospheric pressure.

- 10 Suitable R substituents can comprise lower alkyl groups, i.e., C<sub>1</sub>-C<sub>6</sub> alkyl. Examples of such compounds include 2-methyl-1,4-diazabicyclo[2.2.2] octane; 2,5-dimethyl-1,4-diazabicyclo[2,2,2] octane; 2,6-dimethyl-1,4-diazabicyclo[2.2.2]octane, 2-ethyl-1,4-
- 15 diazabicyclo[2.2.2]octane; 2,5,7-trimethyl-1,4-diazabicyclo[2.2.2]octane; and 2-propyl-1,4-diazabicyclo[2.2.2]octane. These alkyl-substituted compounds are described in the patent literature in U.S. Patent Nos. 3,297,701 (Brader et al, 1967) and 3,325,547 (Cour-
- 20 et al, 1967); British Patent No. 1,045,091 (Farkas et al, 1966); and German Offen. No. 2,215,474, the teachings of which, in regard to the syntheses and properties of these compounds, are hereby incorporated by reference. Alternately, charcoal may be impregnated with an
- 25 aqueous mixture containing a tertiary amine (such as diazabicyclo[2.2.2]octane) and an inorganic salt of iodine or bromine, as described in U.S. Patent No. 4,040,802. (Dietz et al, 1977).
- German Offen. 2,629,302 (Dabby, 1977) reveals the
- 30 use of impregnant compounds substituted with lower alkyl groups, such as 2-methyl-1,4-diazabicyclo[2.2.2]octane,



-4-

applied to the adsorbent material alumina. However, the process of applying the impregnant to the alumina is complex and wasteful. In addition, that document does not disclose information about the kinetics of the adsorption reaction, e.g., the rate at which gas is diffused through the material and the rate at which the alkyl halides are adsorbed on the impregnated alumina. Rapid adsorption rates are very important in the use of adsorbents to remove radioactive molecules from nuclear reactor off-gases.

#### Disclosure of the Invention

The invention described herein arises out of the discovery that several surprising and very useful results occur when 1,4-diazabicyclo[2.2.2]octane, which has been substituted to make it a liquid at room temperature and atmospheric pressure, is applied to charcoal that is used as an adsorbent for radioactive gases. These advances are substantially superior to the prior art regarding both unsubstituted 1,4-diazabicyclo[2.2.2]octane, used as an impregnate on charcoal, as well as substituted 1,4-diazabicyclo[2.2.2]octane used as an impregnate on alumina.

The first surprising advantage relates to the process of applying the impregnate to the adsorbent. When applying substituted 1,4-diazabicyclo[2.2.2]octane, German Offen. 2,629,302 required the adsorbent to be pre-heated under a vacuum, cooled, treated with excess impregnate, and allowed to stand for an hour. The excess impregnate was then removed, by an undisclosed process. The sorbent was then dried for several hours in a vacuum oven; presumably, impregnate that evaporated during that period was either recycled or disposed of.

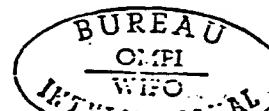


-5-

Unexpectedly, it has been discovered that the process of applying substituted 1,4-diazabicyclo[2.2.2]octane to charcoal is a great deal simpler than the process of applying this same material to alumina. This apparently results from very substantial differences between the pore structure within and diffusion rates through the two adsorbents. The inventors have discovered that the application of substituted 1,4-diazabicyclo[2.2.2]octane does not require pretreatment of the adsorbent with heat and vacuum, nor the use of excess impregnate, nor the removal of excess impregnate. Instead, substituted 1,4-diazabicyclo[2.2.2]octane can be applied to charcoal through a single operation, such as conventional spraying. If the impregnate is simply sprayed over charcoal adsorbent, it will tend to diffuse by capillary action, forming a relatively uniform thin film on very large areas of the charcoal. This is in marked and unexpected contrast to the diffusion of the same compound when applied to alumina.

Several other fluid application techniques can also be used to apply substituted 1,4-diazabicyclo[2.2.2]octane to charcoal. For example, the impregnate could be vaporized and allowed to condense upon the adsorbent. Alternately, the charcoal could be immersed fully or partially in the impregnate, which would coat the charcoal by capillary action.

The second major advantage of using charcoal rather than alumina results from the fact that charcoal has a much greater surface area than the same quantity of alumina. A gram of high-quality charcoal has a total surface area of approximately 1,000 to 1,500 square meters, while a gram of adsorbent alumina has a surface area of approximately 100 to 350 square meters. Therefore, charcoal will tend to retain more impregnate and more radioactive molecules than will alumina.



Another benefit which can be obtained by employing charcoal instead of alumina derives from the fact that charcoal is relatively more hydrophobic than alumina. Therefore, both impregnate molecules and alkyl halides will tend to adsorb more readily to charcoal than to alumina in the presence of substantial humidity, a condition which normally exists in the nuclear reactor uses contemplated by this invention. Impregnate molecules and alkyl halides will also tend to bond more tightly to charcoal than to alumina, thereby being retained more efficiently in the adsorbent bed.

A still further surprising result obtained by using charcoal rather than alumina as adsorbent material is the rate at which radioactive molecules cling to impregnated charcoal. As described in the examples below, a gas stream containing radioactive methyl iodide was passed through an impregnated charcoal bed with a contact time of only about one-fourth of a second. However, the impregnated charcoal removed substantially more than 99% of the input methyl iodide.

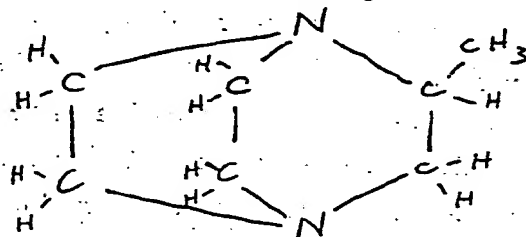
#### Best Mode of Carrying Out the Invention

This invention employs charcoal as an adsorbent material to remove radioactive molecules from gas. The appropriate particle size, bed configuration and dimensions, pretreatment techniques, and other such parameters relating to the use of charcoal in this capacity can be chosen for each application. In general, such parameters will be known to those skilled in the art, or can be determined using no more than routine experimentation.

The charcoal is impregnated with a substituted 1,4-diazabicyclo[2.2.2]octane, wherein the substituent(s) causes the substituted compound to be a liquid at atmospheric pressure and room temperatures.



One preferred impregnant is 2-methyl-1,4-diazabicyclo[2.2.2]octane, which also can be called methyl-triethylene diamine. This substance can be represented by the following formula:



The impregnate is applied to charcoal by any of several conventional fluid handling techniques. A preferred way to apply impregnate to charcoal is by spraying the impregnate with a nebulizer using  
10 air pressure. Impregnation can be accomplished before the charcoal is loaded into an adsorbent bed, or after unimpregnated charcoal is loaded into an adsorbent bed with suitable dimensions and configuration.

Other agents can be added to the specific liquid  
15 impregnant chosen, prior to its application to the charcoal. Similarly, two or more different liquid impregnants according to this invention could be mixed together. It is also possible to dissolve unsubstituted crystalline 1,4-diazabicyclo[2.2.2]octane in  
20 one or more of the liquid impregnants described herein, such as 2-methyl-1,4-diazabicyclo[2.2.2]octane. All such possibilities are included within the scope of this invention.

The amount of impregnate employed for any given  
25 application can vary. In general, amounts between about one percent and about ten percent by weight, based upon the weight of unimpregnated adsorbent, are considered suitable.

Once the impregnated charcoal is loaded into  
30 an adsorbent bed, the bed is installed within a gas handling system using conventional technology. A



preferred way to install an adsorbent bed in a nuclear reactor is to install the bed by means of piping and valves between a source of radioactive gas and an outlet to the atmosphere. Any gas that is released by the reactor to the atmosphere must pass through the adsorbent bed, which removes radioactive molecules from the gas before it is released.

### Example 1

Charcoal derived from a coconut base material, 8/16 mesh, steam activated, and having a surface area of about 1,000 square meters per gram was employed. Before the test began, the charcoal was pre-equilibrated with air at 25°C, 95% relative humidity, in order to obtain reproducible results. About 4.5%, by weight, 2-methyl-1,4-diazabicyclo-[2.2.2] octane was then sprayed upon the charcoal with a nebulizer at about 60 pounds of air pressure. The additional test conditions were:

Temperature - 25°C  
Bed Depth - 2 inches  
Air Velocity - 7.84 inches/second  
Contact time - 0.254 seconds  
Relative humidity - 95%  
Pressure - Atmospheric  
Concentration of radioactively labelled  
Methyl Iodide - 2 mg/meter<sup>3</sup>  
Feed Duration - 2 hours  
Elution Period - 2 hours.

At the end of the four hour test period, 99.92% of the methyl iodide had been retained within the test bed. As much as 3.0% of the methyl iodide could have passed through the charcoal and still met a currently existing commercial standard.

-9-

Example 2

Charcoal impregnated with 2-methyl-1,4-diazabicyclo-[2.2.2]octane, prepared as described in Example 1, was tested at a relatively high temperature. The test conditions were:

Temperature - 130°C  
Relative Humidity - 95%  
Bed Depth - 2 inches  
Air Velocity - 8 inches/second  
Contact time - 0.25 seconds  
Pressure - 42.5 psia  
Concentration of radioactively  
labelled Methyl Iodide - 1.75 mg/m<sup>3</sup>  
Feed Duration - 2 hours  
Elution Period - 2 hours

Under these conditions, the impregnated charcoal retained 99.75% of the input methyl iodide.

Industrial Applicability

The invention described herein has industrial applicability in nuclear power plants and other such applications wherein it is desirable and/or necessary to remove radioactive molecules, such as methyl iodide, from a volume of gas.

Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the embodiments specifically described herein. Such equivalents are intended to be covered by the following claims.



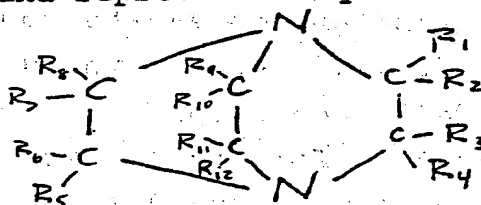
-10-

Claims

1. In the use of charcoal for removing radioactive molecules from gas:

The improvement wherein said charcoal is impregnated with a substituted 1,4-diazabicyclo[2.2.2]octane which is a liquid at room temperature and atmospheric pressure.

2. An adsorbent comprising charcoal impregnated with a compound represented by the structural formula:



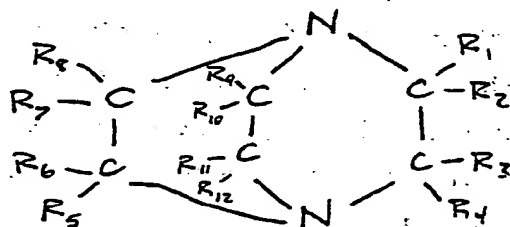
wherein  $R_1$  through  $R_{12}$  are substituents which cause the compound to be a liquid at room temperature.

3. An improvement of Claim 2 wherein at least one of the R substituents comprises a lower alkyl group.
4. An improvement of Claims 2 or 3 wherein one of the R substituents comprises a methyl group and the other R substituents are hydrogen.
5. A charcoal adsorbent impregnated with 2-methyl, 1,4-diazabicyclo[2.2.2]octane.
6. A method for trapping radioactive gaseous products in a gas stream by passing said gas stream through charcoal impregnated with a substituted 1,4-diazabicyclo[2.2.2]octane which is a liquid at room temperature and atmospheric pressure.

BUREAU  
C. F. I.  
100

-11-

7. A method of Claim 6 wherein said substituted 1,4-diazabicyclo[2.2.2]octane is a compound represented by the structural formula:



wherein  $R_1$  through  $R_{12}$  are individually selected from hydrogen and lower alkyl groups.

8. A method of applying an impregnate comprising 1,4-diazabicyclo[2.2.2]octane to an adsorbent comprising the following steps:
- substituting for one or more of the hydrogen atoms on said 1,4-diazabicyclo[2.2.2]octane a substituent group selected so that the resulting compound is a liquid at room temperature and atmospheric pressure; and
  - applying said substituted impregnate to said adsorbent by a technique selected from the following group of techniques: spraying, condensation, partial immersion, and total immersion.
9. An improvement of Claim 8 wherein at least one said substituent group comprises a lower alkyl group.

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 3,491,031	Published	20 January 1970,	1-9
	Stoneburner.			
A	US, A, 4,016,242	Published	05 April 1977,	1-9
	Deitz et al.			
A	US, A, 4,11,833	Published	05 September 1978,	1-7
	Evans.			
A,P	US, A, 4,204,980	Published	27 May 1980,	1-9
	Pasha et al.			

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this International application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

## Remark on Protest

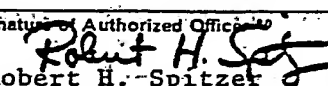
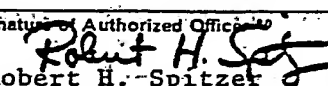
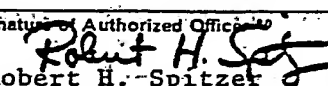
☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US81/00144

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>2</sup> According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL.3 B01D 53/04 U.S. CL. 55/71																													
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border: 1px solid black; padding: 2px; margin: 5px 0;">Minimum Documentation Searched <sup>4</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black; padding: 2px;">Classification System</th> <th style="border: 1px solid black; padding: 2px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">U.S.</td> <td style="border: 1px solid black; padding: 5px;">55/35, 71, 74, 387; 252/428; 521/174; 526/210; 544/351</td> </tr> </table> <div style="text-align: center; border: 1px solid black; padding: 2px; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup></div> <div style="padding: 10px 0;">NONE</div>			Classification System	Classification Symbols	U.S.	55/35, 71, 74, 387; 252/428; 521/174; 526/210; 544/351																							
Classification System	Classification Symbols																												
U.S.	55/35, 71, 74, 387; 252/428; 521/174; 526/210; 544/351																												
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border: 1px solid black; padding: 2px;">Category <sup>6</sup></th> <th style="border: 1px solid black; padding: 2px;">Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup></th> <th style="width: 10%; border: 1px solid black; padding: 2px;">Relevant to Claim No. <sup>18</sup></th> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,040,802 Published 09 August 1977, Deitz et al.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">1-7</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,297,701 Published 10 January 1967, Brader, Jr. et al.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">3-4, 7</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">US, A, 2,818,323 Published 31 December 1957, Haensel.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">8-9</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,015,368 Published 02 January 1962, Reid.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">1-5, 8-9</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,112,320 Published 26 November 1963, Farkas.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">1-5</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,325,547 Published 13 June 1967, Cour-et al.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">1-5</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,429,103 Published 25 February 1969, Taylor.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">1-9</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,453,807 Published 08 July 1969, Taylor.</td> <td style="border: 1px solid black; text-align: center; padding: 5px;">1-9</td> </tr> </table>			Category <sup>6</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>	X	US, A, 4,040,802 Published 09 August 1977, Deitz et al.	1-7	X	US, A, 3,297,701 Published 10 January 1967, Brader, Jr. et al.	3-4, 7	X	US, A, 2,818,323 Published 31 December 1957, Haensel.	8-9	A	US, A, 3,015,368 Published 02 January 1962, Reid.	1-5, 8-9	A	US, A, 3,112,320 Published 26 November 1963, Farkas.	1-5	A	US, A, 3,325,547 Published 13 June 1967, Cour-et al.	1-5	A	US, A, 3,429,103 Published 25 February 1969, Taylor.	1-9	A	US, A, 3,453,807 Published 08 July 1969, Taylor.	1-9
Category <sup>6</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>																											
X	US, A, 4,040,802 Published 09 August 1977, Deitz et al.	1-7																											
X	US, A, 3,297,701 Published 10 January 1967, Brader, Jr. et al.	3-4, 7																											
X	US, A, 2,818,323 Published 31 December 1957, Haensel.	8-9																											
A	US, A, 3,015,368 Published 02 January 1962, Reid.	1-5, 8-9																											
A	US, A, 3,112,320 Published 26 November 1963, Farkas.	1-5																											
A	US, A, 3,325,547 Published 13 June 1967, Cour-et al.	1-5																											
A	US, A, 3,429,103 Published 25 February 1969, Taylor.	1-9																											
A	US, A, 3,453,807 Published 08 July 1969, Taylor.	1-9																											
<div style="font-size: small;"> <sup>15</sup> Special categories of cited documents:            "A" document defining the general state of the art            "E" earlier document but published on or after the international filing date            "L" document cited for special reason other than those referred to in the other categories            "Q" document referring to an oral disclosure, use, exhibition or other means            "P" document published prior to the international filing date but on or after the priority date claimed            "T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention            "X" document of particular relevance         </div>																													
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search <sup>2</sup>            12 May 1981         </td> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report <sup>3</sup>            21 MAY 1981         </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">           International Searching Authority <sup>1</sup>            ISA/US         </td> <td style="border: 1px solid black; padding: 5px;">           Signature of Authorized Officer <sup>19</sup>  <div style="text-align: center;">               Robert H. Spitzer           </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <sup>2</sup> 12 May 1981	Date of Mailing of this International Search Report <sup>3</sup> 21 MAY 1981	International Searching Authority <sup>1</sup> ISA/US	Signature of Authorized Officer <sup>19</sup> <div style="text-align: center;">               Robert H. Spitzer           </div>																							
Date of the Actual Completion of the International Search <sup>2</sup> 12 May 1981	Date of Mailing of this International Search Report <sup>3</sup> 21 MAY 1981																												
International Searching Authority <sup>1</sup> ISA/US	Signature of Authorized Officer <sup>19</sup> <div style="text-align: center;">               Robert H. Spitzer           </div>																												

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL

SECRET

TOP SECRET

CONFIDENTIAL



# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>56684W0003</b>	<b>FOR FURTHER ACTION</b>		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. <b>PCT/US 02/ 05820</b>	International filing date (day/month/year) <b>26/02/2002</b>	(Earliest) Priority Date (day/month/year) <b>10/05/2001</b>	
Applicant  <b>3M INNOVATIVE PROPERTIES COMPANY</b>			

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

DATE 10/1/94 BY SP-10/1/94

RE: [illegible]  
[illegible]  
[illegible]

10/1/94

10/1/94

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/05820

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01J20/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 455 173 A (SECR DEFENCE BRIT) 6 November 1991 (1991-11-06) claims	1-3,7
A	US 4 531 953 A (GROOSE JAMES E ET AL) 30 July 1985 (1985-07-30) cited in the application the whole document	1-3
A	EP 0 143 027 A (FRANCE ETAT) 29 May 1985 (1985-05-29) page 3, last paragraph -page 4, paragraph 1 page 6, line 19 - line 26; claims	1,7
A	WO 81 02256 A (UNDERHILL D; LASKIE J) 20 August 1981 (1981-08-20) page 5, line 1 - line 27	1-3
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## ° Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

23 October 2002

Date of mailing of the international search report

31/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Plaka, T

RECEIVED

1964

1964

1964

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 02/05820

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 792 720 A (LEE HOO-KUN ET AL) 11 August 1998 (1998-08-11) claim 1</p> <p>-----</p>	1-3

1957-1958

1. The first part of the report describes the general situation of the International Geophysical Year (IGY) in 1957-1958. It includes a brief history of the IGY, its objectives, and the participation of various countries. The second part of the report describes the results of the IGY in 1957-1958. It includes a summary of the major scientific achievements, the results of the various expeditions, and the data collected during the year. The third part of the report describes the organization of the IGY in 1957-1958. It includes a list of the participating countries, the names of the scientists and engineers who took part in the IGY, and the names of the various expeditions. The fourth part of the report describes the results of the IGY in 1957-1958. It includes a summary of the major scientific achievements, the results of the various expeditions, and the data collected during the year.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/05820

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0455173	A	06-11-1991	CA 2015810 A1 EP 0455173 A1 US 5145820 A	01-11-1991 06-11-1991 08-09-1992
US 4531953	A	30-07-1985	NONE	
EP 0143027	A	29-05-1985	FR 2553676 A1 DE 3461686 D1 EP 0143027 A1	26-04-1985 29-01-1987 29-05-1985
WO 8102256	A	20-08-1981	CA 1165303 A1 EP 0045318 A1 WO 8102256 A1	10-04-1984 10-02-1982 20-08-1981
US 5792720	A	11-08-1998	KR 155342 B1 JP 2820650 B2 JP 8333109 A	16-11-1998 05-11-1998 17-12-1996

